

A11101 577343

NAT'L INST OF STANDARDS & TECH R.I.C.



A11101577343

/Scientific papers of the Bureau of Stan
QC1 .U572 V22;547-572;1927-28 C.2 NBS-PU

SCIENTIFIC PAPERS
OF THE
BUREAU OF STANDARDS

VOLUME 22
NOS. 547-572

Division ~~IX-0~~

Reference Copy

DEC 14 1928

DENSITY AND ELECTRICAL PROPERTIES OF THE SYSTEM, RUBBER-SULPHUR

By H. L. Curtis, A. T. McPherson, and A. H. Scott

ABSTRACT

Density and electrical properties of compounds of rubber and sulphur were measured for the range of composition from 0 to 32 per cent of sulphur, or from crude rubber to hard rubber. Important changes in the properties with the proportion of sulphur were noted. These changes show definite regularities and occur at compositions which may be represented by simple empirical formulas; they are, accordingly, taken as indicating the existence of definite compounds of rubber and sulphur.

At the composition 19 per cent of sulphur, which corresponds to $(C_6H_8)_2S$, all the properties which have been studied undergo significant changes. At this composition the curve relating density to percentage of sulphur shows a change in slope, and the curve relating thermal expansivity to percentage of sulphur, a distinct inflection. Both the dielectric constant and the power factor curves pass through minima at 19 per cent of sulphur, while the resistivity curve takes a decided upward trend.

The composition 10.5 per cent of sulphur, which corresponds to the formula $(C_6H_8)_4S$, is marked by a maximum value of the dielectric constant. The power factor shows a maximum at 13.5 per cent, which may represent $(C_6H_8)_3S$, or else an equimolecular mixture of $(C_6H_8)_2S$ and $(C_6H_8)_4S$. The maximum of the resistivity occurs at about 26 per cent of sulphur, which corresponds to $(C_6H_8)_4S_3$. Other properties show changes of a less marked nature at these compositions.

No extensive study was made of the effect of free sulphur on the electrical properties of rubber, but data were obtained which indicate that it is small relative to the effect of combined sulphur.

Dielectric strength measurements are not reported because the values seem to depend more on the conditions of test than on the properties of the compounds.

CONTENTS

Part I.—DENSITY OF RUBBER-SULPHUR COMPOUNDS

	Page
I. Introduction	385
II. General plan of the investigation	385
III. Preparation of specimens	386
IV. Method of making density determinations	386
V. Density of unvulcanized mixtures of rubber and sulphur	387
VI. Density of compounds of smoked sheet rubber and sulphur	388
VII. Change in volume accompanying the combination of rubber and sulphur	390
VIII. Density changes in a given stock during vulcanization	392
IX. Density changes in vulcanized rubber on long heating	394
X. Change in density of rubber-sulphur compounds with temperature	396
XI. Conclusions	397

Part II.—ELECTRICAL PROPERTIES OF RUBBER-SULPHUR COMPOUNDS		Page
I.	Introduction	398
II.	Constituents of the system, rubber-sulphur	399
1.	Rubber	399
2.	Sulphur	399
3.	Products of the reaction between rubber and sulphur	400
III.	Preparation of specimens	402
1.	Mixing of stocks	402
2.	Molding of specimens	402
3.	Vulcanization of specimens	403
IV.	Methods of measurement	403
1.	Constant-temperature chamber	404
2.	Mounting of the specimens	404
3.	Leads	404
4.	Dielectric constant	406
5.	Power factor and resistivity	406
V.	Effect of free sulphur on the electrical properties of rubber	406
VI.	Relation of electrical properties to composition	409
1.	Dielectric constant	411
2.	Power factor	412
3.	Resistivity	413
4.	Dielectric strength	414
VII.	Interpretation of the results	415
1.	Formation of definite chemical compounds	416
VIII.	Conclusions	417

Part I.—DENSITY OF RUBBER-SULPHUR COMPOUNDS

By A. T. McPherson

I. INTRODUCTION

This paper presents measurements of the density¹ of compounds of rubber and sulphur over the range of composition from 0 to 32 per cent of sulphur. While the density determinations were undertaken for the very practical purpose of controlling the uniformity of specimens used in another investigation,² the results not only revealed changes which may be of fundamental significance in the reaction between rubber and sulphur, but also supplied data which have direct practical bearing in all cases where the density or the specific gravity of vulcanized rubber is involved.

No systematic or critical investigation on the density of rubber-sulphur compounds is reported in the literature. Glancy, Wright, and Oon³ found a relatively large increase in density on the vulcanization of hard-rubber stocks. Sanderson⁴ observed an increase in density during the vulcanization of soft rubber which he attributed to the elimination of air from the stock rather than to physical change.

II. GENERAL PLAN OF THE INVESTIGATION

Preliminary work indicated that there was a significant increase in density when any mixture of rubber and sulphur was vulcanized, and that this change in density was dependent primarily on the proportion of sulphur which was combined with the rubber rather than on other circumstances. Accordingly, chief emphasis was placed on the measurement of the density of a number of compounds of rubber and sulphur, the composition of which ranged from 0 to 32 per cent of sulphur. These compounds were prepared by vulcanizing mixtures of rubber and sulphur so that practically complete combination took place; no appreciable proportion of free sulphur remained to constitute a variable factor in the composition. To ascertain the

¹ The term "density" is used loosely to include both true and apparent density. By apparent density is understood density based on weighings not corrected for buoyancy of air. Since the densities of the rubber-sulphur compounds here considered are all near the density of water, the correction that would be introduced by considering the buoyant effect of air is relatively small, and, in fact, amounts to only 0.0002 at the greatest. This correction is small in comparison with variations due to other factors, so that qualification of the term "density" would be of academic interest only.

² H. L. Curtis, A. T. McPherson, and A. H. Scott. See Part II of this paper.

³ W. E. Glancy, D. D. Wright, and K. H. Oon, "Rate of combination of sulphur with rubber in hard rubber," *J. Ind. Eng. Chem.*, **18**, pp. 73-75; 1926.

⁴ C. W. Sanderson, "The expansion of rubber compounds during vulcanization," *J. Ind. Eng. Chem.*, **12**, pp. 37-41; 1920.

effect on the density of the conditions of cure, specimens were vulcanized both in an autoclave in open steam and in a vulcanizing press. The time and the temperature of vulcanization were varied within wide limits. Outside of slight secondary changes which occurred on very prolonged curing, no factor was found to affect the density other than the percentages of rubber and sulphur and their state of combination. This being the case, a detailed comparison was made between the density of uncured mixtures of rubber and sulphur on the one hand and on the other the density of the product which resulted on complete vulcanization. The change in density was taken as an accompaniment of the chemical reaction between rubber and sulphur.

A study was made of the density changes in several mixtures of rubber and sulphur at progressive stages of cure, in order to ascertain the relation of the density to time of cure and to the percentage of combined sulphur. The density of several representative compounds was investigated in detail in the last stages of the vulcanizing process in order to determine the magnitude of the changes which might be due to sources other than the reaction between rubber and sulphur. The coefficient of thermal expansion of several compounds was determined in order to reduce the density determinations from the random temperatures at which they were made to a fixed temperature.

III. PREPARATION OF SPECIMENS

Most of the specimens used for density determinations were the ones which had been prepared for electrical tests. The method of mixing the stocks, molding, and vulcanizing the specimens is discussed in Part II of this paper.

IV. METHOD OF MAKING DENSITY DETERMINATIONS

Density determinations were made on strips of convenient size, usually about 5 to 10 g in weight, cut from the previously described electrical test specimens. The method of hydrostatic weighings was ordinarily employed, although the pycnometer method was occasionally used with equally satisfactory results. The usual precautions incident to density determinations were observed. Most of the specimens were quite smooth and no difficulty was encountered in obtaining perfect wetting of the surface.

The variation between determinations on different samples from the same sheet or different sheets from the same batch of stock and the same cure was in most cases only a few parts in 10,000. Where significant variations occurred they were usually large and could be traced to porosity or inhomogeneity that rendered the specimens unsuitable for use. Porosity, even when scarcely apparent to visual

observation, was definitely indicated by a marked reduction in the density and by differences between individual strips. As an illustration of the uniformity that may be expected among good specimens, seven consecutively prepared sheets from a given stock⁵ showed values of the density ranging from 0.9322 to 0.9325, or a maximum variation of 3 parts in 10,000. With higher percentages of sulphur wider variations might be expected on account of the greater difficulty in obtaining uniform mixing. However, the average variation encountered in about 50 determinations on hard rubber was only ± 2 parts in 10,000, when comparison was made between different samples from the same batch and the same cure.

V. DENSITY OF UNVULCANIZED MIXTURES OF RUBBER AND SULPHUR

The density of unvulcanized mixtures of rubber and sulphur was determined experimentally in only a few cases. Good agreement with calculated densities was noted, and it was considered sufficient for the purposes of the present investigation to calculate most of the density values from the experimentally determined density of crude rubber and the known density of rhombic sulphur.

The density at 25° C. for samples from five different lots of smoked sheet rubber varied from 0.9100 to 0.9126 with an average value of 0.9112. One lot of hard, fine Para rubber, washed and dried, had a density of 0.916.

The density of sulphur depends on which allotropic modification is being considered. Rhombic sulphur has been reported to have a density of 2.07, monoclinic sulphur a density of 1.96, while the densities of amorphous modifications are variously given from 1.90 to 2.05. Rhombic sulphur was used in the present investigation. Its density, as determined by experiment, was 2.05.

The density was calculated for mixtures of rubber and sulphur by the simple equation

$$D \text{ (mixture)} = \frac{100}{\frac{X}{D \text{ (rubber)}} + \frac{100-X}{D \text{ (sulphur)}}}$$

where

X = per cent of rubber,

$100 - X$ = per cent of sulphur.

⁵ The composition was—

	Per cent
Pale crêpe rubber	97
Zinc oxide	1
Sulphur	1.75
Tetramethylthiuram disulphide	.25

The specimens were cured for 25 minutes at 127° C.

The curve showing the relation of the density of mixtures to composition is given in Figure 1. This curve is slightly convex with reference to the composition axis.

VI. DENSITY OF COMPOUNDS OF SMOKED SHEET RUBBER AND SULPHUR

The densities of a number of compounds of smoked sheet rubber and sulphur are given in Table 1. Each value given for the density is the average of two or more closely agreeing determinations on

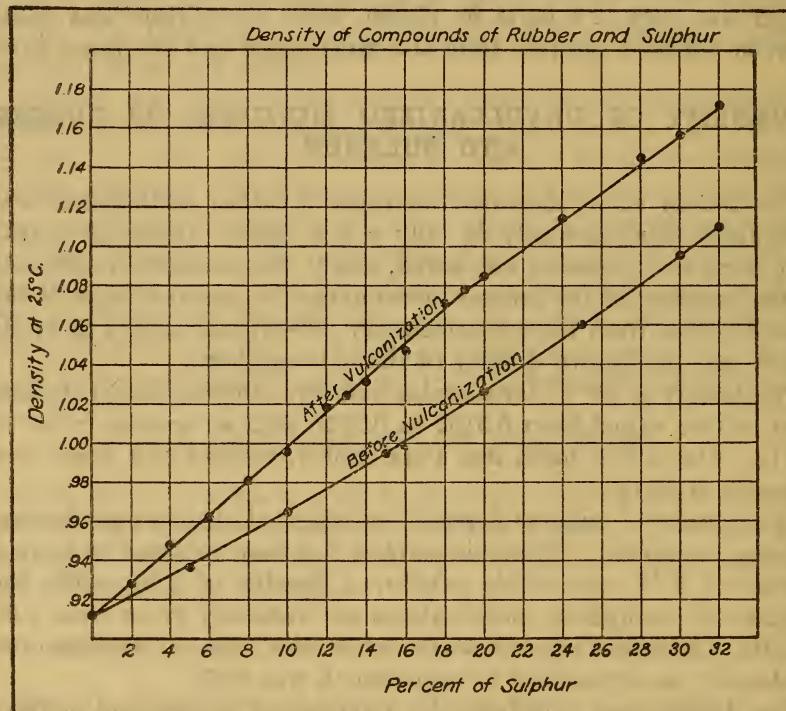


FIG. 1.—Curves showing the density of rubber stocks before and after vulcanization

different strips of the same material. For convenience, the density determinations were made at ordinary laboratory temperatures. They were corrected to 25° C. by the use of coefficients of expansion, which are considered in a separate section of this paper. The state of vulcanization of the compounds considered is indicated not by determinations of combined sulphur, but rather by determinations of the residual or free sulphur.⁶

⁶ The circumstances which frequently render free sulphur determinations inaccurate are not present here, since the uncombined sulphur is completely dissolved in the rubber, and consequently uniformly distributed through it. In no case was there enough free sulphur to cause blooming.

In the table, compounds are grouped according to the percentage of sulphur which they contain, regardless of other considerations, such as time or temperature of cure.

TABLE 1—*The density of compounds of smoked sheet rubber and sulphur*

Composition		Vulcanization		Free sulphur	D_{25}	Average D_{25} for given composition
Rubber (smoked sheet)	Sulphur	Time	Temperature			
Per cent	Per cent	Minutes	°C.	Per cent		
100	0				0.9126	
100	0				.9113	0.912
98	2	600	160	0.04	.9282	.928
96	4	600	160	.02	.9478	
96	4	600	160		.9478	.948
94	6	1,600	141	.04	.9650	
94	6	900	151	.07	.9613	.962
92	8	600	160	.10	.9808	
92	8	600	160		.9816	.981
90	10	600	160		.9956	
90	10	600	151		.9951	.995
88	12	600	160		1.0180	1.018
87	13	600	151		1.0226	
87	13	250	151	.07	1.0247	
87	13	600	141	.09	1.0236	
87	13	160	160	.07	1.0235	
87	13	240	160	.07	1.0245	1.024
86	14	250	151	.05	1.0310	1.031
84	16	160	160		1.0468	1.047
82	18	360	160		1.0716	
82	18	250	151	.09	1.0707	1.071
81	19	360	160		1.0781	1.078
80	20	1,600	141	.09	1.0558	
80	20	900	151	.05	1.0850	1.085
76	24	1,600	141	.06	1.1141	
76	24	900	151	.05	1.1158	1.115
72	28	1,600	141	.07	1.1431	
72	28	2,500	141	.05	1.1445	1.145
72	28	900	151	.18	1.1436	
72	28	1,600	151	.05	1.1454	
71.5	28.5	360	160		1.1458	1.146
70	30	1,600	141	.37	1.1566	
70	30	2,500	141	.15	1.1572	
70	30	900	151	.37	1.1560	1.157
70	30	1,600	151	.20	1.1596	
68	32	1,600	141	.76	1.1701	
68	32	2,500	141	.65	1.1714	1.172
68	32	900	151	1.00	1.1712	
68	32	1,600	151	.69	1.1726	

A comparison of the density values at different times and temperatures of vulcanization warrants this grouping since the agreement is, on the average, within about 1 or 2 parts in 1,000. This is in spite of the fact that the specimens compared were differently cured and were made at different times and from various lots of smoked sheet. However, the state of vulcanization of specimens, in terms of sulphur combined with rubber, did not vary greatly from one specimen to another, since the residual, or free sulphur, was generally between 0.05 and 0.10 per cent. Only in the case of compounds containing 28 to 32 per cent of total sulphur was the free sulphur somewhat higher.

While no indication is given in the table as to the method of vulcanization, some specimens were cured in open steam in an autoclave, and others in a vulcanizing press. In many cases the press was used without applied hydraulic pressure. There was no evidence that the pressure under which the specimens were cured had a significant effect on their density.

Aside from the state of combination of rubber and sulphur, the only circumstance that was found to have an effect on the density was the time of vulcanization at a given temperature. Long heating after the combination of rubber and sulphur is practically complete increases the density. This increase is not large, but it may be somewhat greater than the experimental error in making determinations and in reproducing batch compositions. Density changes from this source are considered in a separate section of this paper, since they are of a lower order of magnitude than the changes that accompany the main reaction between rubber and sulphur.

Leaving secondary density changes out of consideration, for the present, average values of the density of vulcanized rubber of different compositions, rounded off to the third decimal place are given in Table 1. In Figure 1 these values of density are plotted against the composition. The relation is better represented by two straight lines meeting at the composition, 19 per cent of sulphur, than by a smooth curve. It is possible that more accurate determinations would show a different relation.

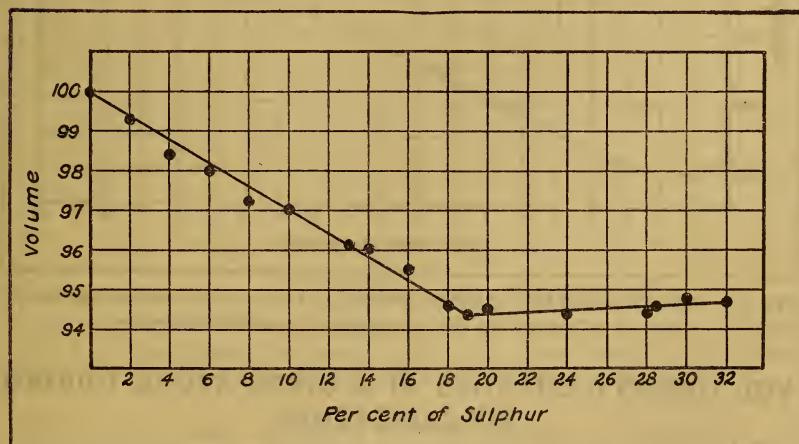
VII. CHANGE IN VOLUME ACCOMPANYING THE COMBINATION OF RUBBER AND SULPHUR

A comparison of the curve for the density of smoked sheet-sulphur compounds with that for the density of unvulcanized mixtures indicates the magnitude of the decrease in volume which accompanies vulcanization. As may be noted by reference to Figure 1, the density change is quite appreciable even for low proportions of sulphur, while with higher proportions of sulphur it amounts to several units in the second decimal place. The curves for the density before and after vulcanization do not have the same shape so the volume change is not a simple uniform function of the composition.

There are several possible ways of expressing the density or the volume change, depending upon the particular comparisons which are to be made. For many reasons a convenient and useful relation is that which is obtained when the volume of the product from the vulcanization of 100 volumes of different rubber-sulphur mixtures is plotted against the composition. The data expressed in this form are shown in Figure 2 and in Table 2. The curve in the figure is drawn as two straight lines meeting at a point. The data are only in moderately good agreement with this arrangement, but they are not of sufficient accuracy to define a more complicated curve, which might better express the true relationship involved.

TABLE 2.—*The change in volume accompanying the vulcanization of rubber-sulphur mixtures*

Composition		Density D_{25}	Volume resulting from the vulcanization of 100 volumes of rubber-sulphur mixture
Sulphur	Atoms of sulphur per (C ₆ H ₅)		
<i>Per cent</i>			
0	0	0.912	100
2	0.043	.928	99.3
4	.089	.948	98.4
6	.136	.961	98.0
8	.185	.981	97.2
10	.237	.995	97.0
10.5	.250		
13	.319	1.024	96.1
13.5	.332		
14	.346	1.031	96.0
16	.405	1.047	95.5
18	.467	1.071	94.6
19	.499	1.078	94.4
20	.531	1.085	94.5
24	.671	1.115	94.4
28	.827	1.145	94.4
28.5	.846	1.146	94.6
30	.911	1.157	94.8
32	1.000	1.172	94.7

FIG. 2.—*Curve indicating the change in volume of rubber-sulphur stocks on vulcanization*

Ordinates are the volumes of the compounds which result from the vulcanization of 100 volumes of rubber-sulphur mixtures.

It is apparent from this curve that the volume change attendant on the formation of soft-rubber compounds is significant. For instance, the combination of 3 per cent of sulphur brings about a shrinkage of 1 per cent in volume, or a corresponding increase in density. The largest relative volume change is that which accompanies the combination of rubber with 19 per cent of sulphur. This amounts to a little less than a 6 per cent reduction in volume. For

the range of hard-rubber compounds the volume change is about the same as for the 19 per cent compound.

The striking feature of the curve given in Figure 2 is the break or point of inflection which occurs at the composition, 19 per cent of sulphur. As indicated in Table 2, this composition corresponds to one-half an atom of sulphur for each C_5H_8 group or to a formula, $(C_5H_8)_2S$. This break is distinct and reasonably sharp. Coming as it does at a composition represented by a simple formula, it would seem to have important significance in interpreting the reaction between rubber and sulphur. A discussion of this is given in Part II of this paper.

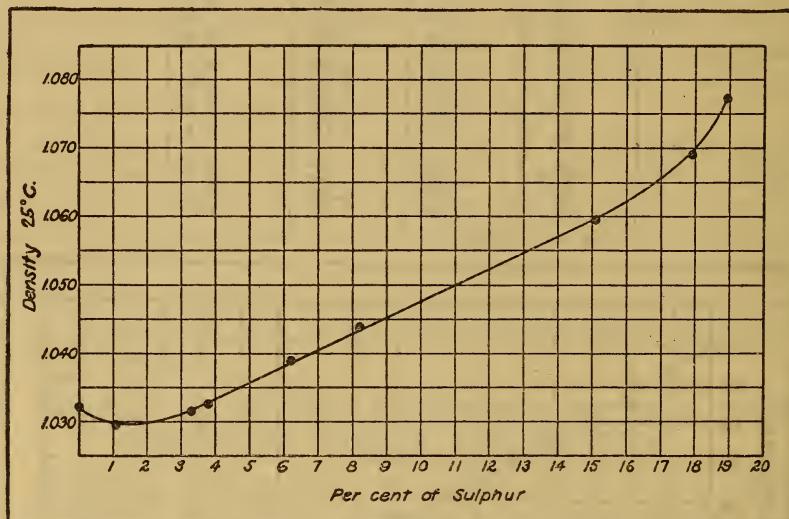


FIG. 3.—Curve showing the change in density of a given stock during vulcanization as a function of the percentage of combined sulphur

VIII. DENSITY CHANGES IN A GIVEN STOCK DURING VULCANIZATION

The previous discussion considers the density of rubber-sulphur stocks only at initial and final stages of vulcanization. A few stocks were examined at progressive stages of cure to ascertain the way in which the change in density takes place relative to the time of cure and the proportion of combined sulphur. When a large proportion of sulphur is used in a rubber-sulphur mix, the specimens obtained at short cures are frequently unsatisfactory for accurate density determinations on account of the blooming of the free sulphur. Some stocks, however, gave specimens which were free from objectionable blooming for a considerable time, even though a large pro-

portion of free sulphur were present. The following is one of such stocks which was studied in some detail.

	Parts by weight
Rubber	81
Zinc oxide	1
Sulphur	19
Tetramethylthiuramdisulphide	1
Total	102

Including the sulphur in the accelerator, this stock contained 19.1 per cent of sulphur, which is half the maximum proportion that can react with rubber.

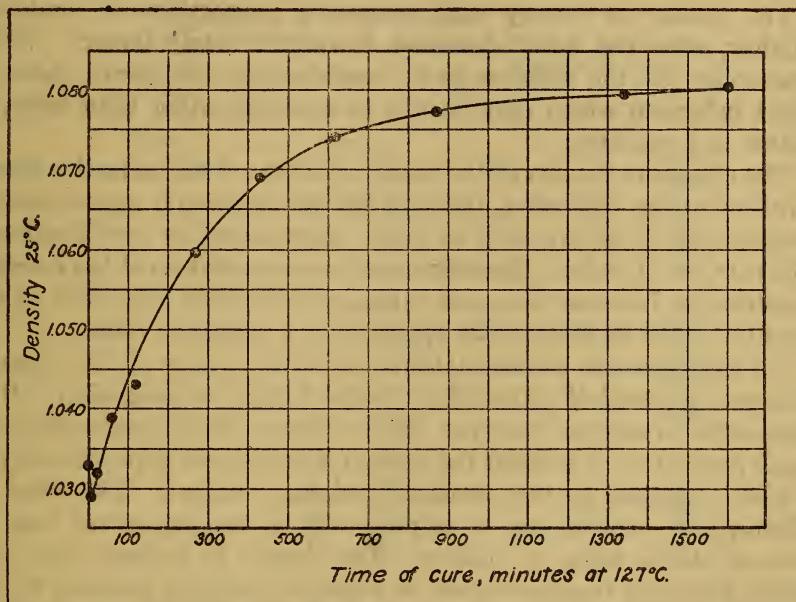


FIG. 4.—Curve showing the change in density of a given stock during vulcanization as a function of the time of vulcanization

The density and combined sulphur content of specimens of this stock at different cures are given in Table 3, and are shown graphically in Figures 3 and 4. At short times of vulcanization there is a small but distinct decrease in density which is probably due to a change in the large proportion of free sulphur that is present from the rhombic modification to less dense allotrophic modifications. This explanation of the initial decrease in density is supported by the fact that slow, rather than abrupt, cooling of specimens from vulcanizing temperatures, allowing them to stand at room temperature, or otherwise treating them in a way which would favor the transformation of the sulphur to the rhombic modification, increased their density.

TABLE 3.—*The change in density of a rubber-sulphur stock¹ during vulcanization*

Time of vulcanization (minutes at 127° C.)	Com- bined sulphur	Density (25°)	Time of vulcanization (minutes at 127° C.)	Com- bined sulphur	Density (25°)
0.....	<i>Per cent</i>	2 1.0322	270.....	<i>Per cent</i>	15.1 1.0597
2.....	1.1	1.0295	430.....	17.9	1.0690
8.....	3.3	1.0313	615.....		1.0743
13.....	3.8	1.0325	870.....	18.9	1.0772
20.....	3.7	1.0328	1,340.....		1.0793
60.....	6.2	1.0389	1,600.....		1.0802
90.....	8.2	1.0438			

¹ See text for composition.² Density calculated from composition, 1.0327.

The change in density with increasing proportions of combined sulphur, after the initial decrease, is approximately linear. When practically all the sulphur is in combination, the curve shows a slight inflection which may be due to reactions other than between rubber and sulphur.

The change in density of the stock with time of vulcanization shows an offset at the beginning, and then follows the general course that the reaction would be expected to follow from mass law considerations. The rate, rapid at first, diminishes as the concentration of the reacting constituents becomes less, and ultimately becomes very slow as the density makes an asymptotic approach to a constant value.

No experimental determinations have been made of the density changes in practical soft-rubber stocks during vulcanization. It is reasonable to assume, however, that for stocks containing a relatively small proportion of sulphur the density will increase approximately as a linear function of the combined sulphur content. The effect of allotropic transformation of sulphur will be less important than in case of stocks high in sulphur. The change in volume that may result from the transformation of sulphur from the rhombic to the amorphous form is about 7 or 8 per cent of the volume of the sulphur. The change in volume accompanying the reaction of rubber with a small proportion of sulphur, however, is about 75 per cent of the volume of the sulphur, or fully ten times as much as the effect of allotropic change.

IX. DENSITY CHANGES IN VULCANIZED RUBBER ON LONG HEATING

The density changes of several compounds at long times of cure were studied in order to ascertain the effect on the density of the combination of the last portions of the sulphur, and to determine the magnitude of any secondary changes which might be due to factors other than the reaction between rubber and sulphur. The compositions considered ranged from 6 to 32 per cent of sulphur; specimens were prepared at each of two temperatures. The density

and free sulphur content of specimens of three of these compounds are shown in Table 4. For the density determinations of the specimens vulcanized at 141°, the same pieces of rubber were used at all four times of cure. After the first density determinations the test strips were dried and then given the second stage of cure by heating them in nitrogen. After the second series of density measurements, this process was repeated for the third and the fourth cures. For the determinations with specimens vulcanized at 151°, individual specimens were prepared at each cure.

TABLE 4.—*Density of rubber-sulphur compounds near the completion of vulcanization*

Composition		Vulcanization		Free sulphur	Density D_{25}
Smoked sheet	Sulphur	Time	Temperature		
Per cent 94	Per cent 6	Minutes 600 1,000 1,600 2,500 300 600 900 1,600	°C. 141 141 141 151 151 151 151 151	Per cent 0.06 .04 .10 .07	0.9600 .9617 .9630 .9645 .9605 .9606 .9613 .9617
					1.0801 1.0843 1.0858 1.0876 1.0800 1.0854 1.0850 1.0869
					1.1680 1.1697 1.1700 1.1714 1.1687 1.1720 1.1712 1.1726
80	20	Minutes 600 1,000 1,600 2,500 300 600 900 1,600	°C. 141 141 141 151 151 151 151 151	Per cent .23 .09 .24 .05	1.0801 1.0843 1.0858 1.0876 1.0800 1.0854 1.0850 1.0869
68	32	Minutes 600 1,000 1,600 2,500 300 600 900 1,600	°C. 141 141 141 151 151 151 151 151	Per cent 1.17 .76 .65 2.01 1.01 .64	1.1680 1.1697 1.1700 1.1714 1.1687 1.1720 1.1712 1.1726

There is no significant difference between results at the two temperatures when equivalent periods of time are considered.

There is no apparent relation between the density increase on prolonged vulcanization and the accompanying small decrease in residual sulphur content. For instance, as large a density increase occurs in the case of the 6 per cent sulphur compound with a reduction of the residual sulphur of only 0.03 per cent as occurs in the 30 or 32 per cent sulphur compounds when over 1 per cent of residual sulphur is brought into combination on long heating.

Without further investigation little can be said as to the cause of these changes in density on long heating, beyond the supposition that they may be due to reactions of the nonhydrocarbon constituents of the rubber. The magnitude of the effect on the density of vulcanized rubber is of the order of two or three units in the third decimal place. This effect is small in comparison with the

change in density due to vulcanization, but with reference to the precision which can easily be attained in making density determinations it is very large. In view of this limitation there has been no effort in the present investigation to attain a high order of precision from the standpoint of density measurement.

X. CHANGE IN DENSITY OF RUBBER-SULPHUR COMPOUNDS WITH TEMPERATURE

Density determinations were made at laboratory temperatures which varied between 20 and 30° C. In order to correct these

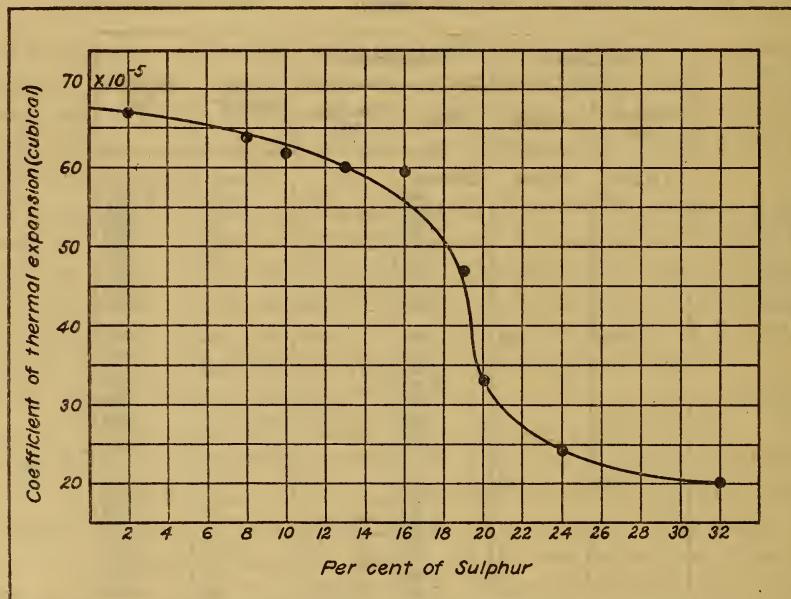


FIG. 5.—Curve showing the coefficient of thermal expansion of rubber-sulphur compounds

determinations to a standard temperature, 25° C., the change in density with temperature was determined for several compounds. The range considered was from about 15 to 40° C. Within these limits the density of most compounds could be represented as a linear function of the temperature with sufficient accuracy for the present purpose of correcting density determinations to a standard temperature.

Coefficients of thermal expansion for the various compounds were computed from the changes in density with temperature. These coefficients are given in Table 5 and are shown by the curve in Figure 5. The coefficients for soft rubber are much larger than those for hard rubber. The transition is not gradual, but the important change occurs near the composition 19 per cent of sulphur.

TABLE 5.—*Coefficients of thermal expansion of rubber-sulphur compounds*

Composition		Coefficient of cubical expansion
Rubber	Sulphur	
Per cent	Per cent	
98	2	67×10^{-6}
92	8	64×10^{-6}
90	10	62×10^{-6}
87	13	60×10^{-6}
84	16	59×10^{-6}
81	19	47×10^{-6}
80	20	33×10^{-6}
76	24	24×10^{-6}
68	32	20×10^{-6}

Coefficients of thermal expansion for rubber given in the literature are not applicable in the present connection because they generally refer to samples of unknown or unspecified composition, whereas the above results indicate that composition is significant.

XI. CONCLUSIONS

A substantial increase in density accompanies the vulcanization of rubber with sulphur. The volume change is due to chemical reaction between rubber and sulphur. The density of a compound of rubber and sulphur, is, therefore, a function of its composition. The density is independent of the means used to effect combination of rubber and sulphur, except that long heating after the reaction is practically complete causes a slight increase in density which is apparently due to secondary reactions.

The relation between density and composition may be represented approximately by a linear curve with a discontinuity in slope at 19 per cent of sulphur, the composition which corresponds to half the maximum proportion of sulphur with which rubber can combine.

The volume change accompanying the vulcanization of rubber-sulphur mixtures increases with increasing proportion of sulphur up to 19 per cent. From this composition to 32 per cent of sulphur the volume change is approximately constant.

The density changes which occur during the vulcanization of a given stock are not simple; one complicating factor is the transformation of the sulphur to allotropic modifications of different density. In general, the density change on vulcanization of a stock containing 19 per cent of sulphur bears a linear relation to the proportion of combined sulphur; with time of cure, the density increases rapidly at first, then more slowly, and ultimately makes an asymptotic approach to a constant value.

The coefficient of thermal expansion of rubber-sulphur compounds decreases with increasing sulphur content, but not in a linear manner.

WASHINGTON, April 27, 1927.

Part II.—ELECTRICAL PROPERTIES OF RUBBER-SULPHUR COMPOUNDS

By H. L. Curtis, A. T. McPherson, and A. H. Scott

I. INTRODUCTION

This paper represents a systematic study of the effect of vulcanization on the electrical properties of rubber. Dielectric constant, power factor, and resistivity were measured over the entire range of composition in which rubber may combine with sulphur. The electrical properties show regularities which suggest the existence of several definite chemical compounds of rubber and sulphur.

The published data on the electrical properties of rubber-sulphur compounds relate, in general, to ranges of composition between 2 and 10 per cent, and between 25 and 32 per cent of sulphur, the former being associated with soft rubber and the latter with hard rubber. Moreover, in many cases data on the electrical properties of rubber are cited in which the effect of vulcanization with sulphur is not differentiated from the effect of adding other constituents. In a previous investigation,¹ however, it was noted that the dielectric constant and power factor of soft rubber increased with the per cent of sulphur and reached values which were decidedly higher than those ordinarily assigned to hard rubber. This indicated that these properties must have maximum values in the region of composition between soft and hard rubber. The results herein reported show that as the percentage of sulphur is increased beyond that used in the vulcanization of soft rubber, both the dielectric constant and the power factor pass through maxima, and then, with still more sulphur, pass through minima before the hard-rubber stage is reached.

When several different properties have a maximum or a minimum value at the same point in the composition curve, the existence of a definite chemical compound is indicated. On this basis the electrical properties indicate that the following compounds² exist; $(C_5H_8)_4S$, $(C_5H_8)_2S$, $(C_5H_8)_4S_3$, and possibly $(C_5H_8)_3S$.

¹ H. L. Curtis and A. T. McPherson, Dielectric Constant, Power Factor, and Resistivity of Rubber and Gutta-Percha. B. S. Tech. Papers, 19, p. 699; 1925. (No. 299.)

² Simple formulas are here employed without the use of subscripts to denote that the molecules may be polymers. The present discussion is not concerned with the size or with the structural formulas of molecules of rubber-sulphur compounds.

II. CONSTITUENTS OF THE SYSTEM, RUBBER-SULPHUR

The rubber-sulphur system is not as simple as many of the familiar two-component systems of metallurgy or inorganic chemistry. One of the components (rubber) is complex and contains a main constituent with several minor constituents in appreciable amounts. The reaction between rubber and sulphur does not proceed to an equilibrium, so the nature of the product may depend on the conditions of the reaction. The phase rule, that tool which is invaluable in the study of many systems, is not applicable to the one under consideration.

1. RUBBER

Natural gum rubber was used throughout the present investigation. While the chief constituent is rubber hydrocarbon, yet other constituents are not negligible in amount or in their effect on the properties. In high-grade plantation rubber proteins are present to the extent of 2 or 3 per cent; resins occur in about the same proportion, and other constituents are found in smaller amounts. The resins have a very pronounced effect on the rate of reaction between rubber and sulphur, as well as on the tensile properties of the resulting vulcanized rubber. There are no data relating to the effect of the nonhydrocarbon constituents on the electrical properties of rubber.

The use of natural gum rubber, rather than of pure rubber hydrocarbon, as a component in the investigation of the rubber-sulphur system was a matter of practical expediency. Crude rubber is a well-standardized and abundantly available material; its composition is reasonably constant. The results obtained with it are directly applicable to practical rubber compounds, and at the same time they give indication as to the nature of the reaction between rubber hydrocarbon and sulphur.

2. SULPHUR

When sulphur is mixed with crude rubber a small proportion of it goes into solution, and sulphur in excess of this is simply dispersed through the rubber. When the mixture of rubber and sulphur is heated to the temperature of 120 to 160° C. for vulcanization, the solubility of sulphur is materially increased. The sulphur, dispersed as particles, tends to dissolve in and diffuse through the rubber so as to give a uniform solution. But at the same time a reaction is taking place between the dissolved sulphur and the rubber. Whether the vulcanized rubber produced is perfectly homogeneous or not depends on the speed of diffusion of sulphur as compared with the rate of reaction. If the heating is continued for a sufficiently long time, practically all of the sulphur may go into combination with the

rubber, provided, of course, that the amount of sulphur that was taken did not exceed 32 per cent. However, in the manufacture of practical rubber goods the process is usually interrupted when only part of the sulphur has reacted. The uncombined sulphur, if present in small proportion, will remain dissolved in the vulcanized rubber; but if larger amounts are present, particles of solid sulphur will be found interspersed through the rubber when it is cooled, and a characteristic sulphur "bloom" will appear on the surface.

In this investigation common practice has been followed in regarding sulphur that can be extracted by acetone as "free sulphur," and sulphur that can not be extracted as being in combination with the rubber hydrocarbon. This may not be exactly correct. If sulphur should react with resins and proteins which are present in natural rubber along with the hydrocarbon, then that portion of sulphur in products soluble in acetone would be classed as "free," and the portion in products not soluble in acetone would be classed as "combined."

Most of the specimens prepared in the course of this investigation were vulcanized until practically all of the sulphur was brought into combination. It is not possible to effect the combination of all of the sulphur in a reasonable time, because the rate of reaction of sulphur becomes very slow as the concentration becomes low, as would be expected from mass-law considerations. The amount of free sulphur was determined for many of the specimens. It was, in general, less than 0.1 per cent on the basis of the whole specimen. Larger amounts were found only in the specimens that contained from 28 to 32 per cent of total sulphur. In these specimens the free-sulphur content ranged up to about 1 per cent.

3. PRODUCTS OF THE REACTION BETWEEN RUBBER AND SULPHUR

It is well established by numerous analytical investigations that the composition of rubber hydrocarbon may be represented by the formula $(C_5H_8)_x$, and further, that the composition of vulcanized rubber containing the maximum proportion of sulphur in combination is $(C_5H_8S)_y$. Various physical data indicate that both x and y are very large. Between these two extremes of composition rubber combines with sulphur in any proportion. The existence of definite compounds of intermediate composition has been suggested at various times, but no sufficiently convincing evidence has been adduced to lead to the general recognition of any of them. It is commonly supposed that the reaction between rubber and sulphur gives a continuous series of products, the properties of which, along with the composition, change in a regular and gradual way from soft rubber containing 2 to 4 per cent of combined sulphur to hard rubber containing about 32 per cent. This series is regarded as

being practically infinite, with no compound or compounds that stand out so as to be recognizable as definite chemical individuals having characteristic properties.

This supposition of a series of compounds, each differing from the other by an imperceptible amount, involves the assumption that as sulphur atoms combine with the molecule of rubber hydrocarbon the positions available for the attachment of sulphur are filled in a random fashion from first to last. It leaves out of consideration the recognized principle of organic chemistry that a reaction in one part of a molecule influences to some extent the reactivity of the whole molecule, and particularly the reactivity of adjacent parts, so that successive steps in a reaction between two substances which combine in more than one proportion, take place not in a random but in an orderly fashion. As an example, in the familiar case of benzene all six carbon atoms in the molecule are equivalent, but as soon as one of them becomes the point of attachment of a substituted radical, then the relative positions that will be taken by subsequently introduced substituents are definitely determined. If all parts of the molecule of rubber hydrocarbon are regarded as equivalent, then at the outset of the reaction with sulphur the positions taken by the first sulphur atoms entering into combination would be determined largely by chance. But as a moderate proportion of the available positions should become filled, then subsequent additions of sulphur atoms would be more and more strongly influenced by those already in the molecule, and an orderly arrangement of sulphur atoms among the available positions would tend to come about. If, for illustration, the very simple assumption be made that a sulphur atom attached to one position in the rubber molecule renders more difficult the addition of sulphur to two immediately adjacent positions, then vulcanization with a large proportion of sulphur would lead to the formation of a definite compound in which practically every alternate position would be filled. After the conversion of all of the rubber to this compound, then the reaction would proceed at a different rate to the formation of the well-known completely saturated compound. The actual case is probably not so simple as this, because the effect of sulphur in one position in the molecule might reasonably extend to several adjacent positions.

From considerations such as these it is reasonable to expect that the reaction of rubber with sulphur would produce, at the outset, an almost continuous and undifferentiated series of compounds since the relatively few sulphur atoms would have an almost random distribution among the relatively large number of available positions at which they might combine, but with increasing proportion of sulphur entering into combinations definite compounds would emerge and the reaction would tend to become stepwise instead of continuous.

It is not possible to predict the composition at which first evidences of definite compound formation would appear, but they would likely be most distinct at about the halfway point in the reaction.

III. PREPARATION OF SPECIMENS

The preparation of samples was given careful consideration both from the standpoint of making vulcanized rubber of known composition that would be uniform and free from defects and from the standpoint of making specimens of form and dimensions which would render them best adapted to electrical measurement.

1. MIXING OF STOCKS

The mixing of stocks was conducted with care, since the composition was controlled by the amounts of rubber and sulphur taken rather than by subsequent analysis of the products. The rubber was weighed both before and after mastication, or "breaking down," on heated rolls of the mixing mill. At the temperature of about 110° C., which was ordinarily employed, there was a loss of about 0.3 or 0.4 per cent of moisture and other volatile constituents from the smoked sheet rubber which was used in this investigation. The rubber was cooled to about 70° C. and sulphur, in weighed amounts, was added by sifting while the rubber was being worked on the mixing mill. The mixture of rubber and sulphur was weighed and additional sulphur was added, if necessary, to make up for any loss by dusting. The compounding was probably accurate to within 1 part of 1,000. Density determinations, which are reported in Part I of this paper, served as a check on the uniformity of specimens.

The consistency of density determinations from one composition to another indicated that no serious errors were made in compounding. The analysis of several specimens at the conclusion of the investigation gave percentages of sulphur that were in good accord with the percentages of sulphur as compounded.

2. MOLDING OF SPECIMENS

Specimens were prepared for electrical measurement by molding them to a suitable shape before they were vulcanized. Specimens containing less than 16 per cent of sulphur were easily molded with embedded electrodes after the manner described in a previous publication.³ In the case of compositions containing higher proportions of sulphur, however, the aluminum plate electrodes did not adhere well to the rubber after vulcanization. The difficulty was overcome by removing the aluminum plates altogether and painting

³ See footnote 1, p. 398.

with conducting lacquer⁴ the faces of the rubber specimens which were left recessed by the removal of the plates. This simply meant the substitution of a conducting paint film for the aluminum electrodes.

When stocks high in sulphur were molded at the temperatures commonly used for vulcanization, 140 to 160° C., the sulphur did not remain uniformly dispersed throughout the rubber, but collected into droplets which, from their relatively greater mobility, tended to flow to the outside of the sheet during the molding. This resulted in specimens that were not homogeneous. The difficulty was avoided by molding the specimens at a temperature somewhat below the melting point of sulphur.

3. VULCANIZATION OF SPECIMENS

The vulcanization of specimens was carried out either in open steam in an autoclave or in a vulcanizing press between platens which were separated by a spacing ring equal in thickness to the specimen. In either case, specimens were covered with aluminum foil to further protect them from the action of steam or air.

At the beginning of the investigation some of the specimens became porous on vulcanization. The cause of this was found to be moisture in the rubber. When a mixing procedure was adopted in which there was a hot breakdown of the crude rubber no further difficulty was encountered from this source.

IV. METHODS OF MEASUREMENT

The methods of measurement are substantially those described in a previous paper.⁵ However, the measurements there reported were made at room temperatures and at undetermined humidities, whereas the measurements herein reported have all been made at 25° C. and less than 1 per cent relative humidity. To make measurements under these conditions has required a special mounting for the specimens in a constant temperature chamber and slight modifications in the electrical measurements.

⁴ The method of making conducting paint was developed from directions given by James, *Elect. World*, 67, p. 51; 1916. Experiments indicated that the precipitation, washing, and resolution of the paint in James's procedure simply amounted to the addition of a small proportion of hydrochloric acid, so the following simpler recipe was used: *Mix bronze powder with twice its weight of celluloid lacquer, add 5 to 10 per cent, by weight of concentrated hydrochloric acid with vigorous stirring, and apply within a few minutes.* The lacquer may be made by dissolving clear celluloid, 1 part, in a mixture of 10 parts of acetone and 10 parts of amyl acetate, or in a similar solvent. Commercial nitrocellulose lacquer may be used if 3 to 5 per cent of camphor is added to make it equivalent to celluloid lacquer. In the absence of camphor the paint is nonconducting. Several different bronze, or "gold" powders of varying color and composition were found to be equally satisfactory, but aluminum powder was not satisfactory. Thorough drying of specimens to which painted electrodes had been applied was found to be necessary, since traces of the lacquer solvent dissolved in rubber may have a marked effect on the electrical properties. The power factor is particularly sensitive to contaminations of this sort.

⁵ See footnote 1, p. 398.

1. CONSTANT TEMPERATURE CHAMBER

The constant temperature chamber consisted of the lower half of an earthenware jar, about 55 cm high and 43 cm in diameter. A hard rubber disk having a diameter slightly less than the jar rested on a ledge which was fastened inside the jar at about half its height. This disk served as a cover for the chamber, and could be sealed in place with paraffin so as to render the chamber practically airtight. The jar was set in an oil bath which was maintained at the desired temperature by a thermostat. The air in the chamber was stirred by a fan which was driven by a motor located outside. A tray of concentrated sulphuric acid in the bottom of the chamber kept the humidity very low.

2. MOUNTING OF THE SPECIMENS

The specimens were placed on a hard rubber disk which was suspended by rods from the hard rubber cover of the constant temperature chamber. As the leads to the specimens passed through the cover, the specimens could be completely mounted before lowering into the chamber. Each specimen had two concentric electrodes, one 22 cm in diameter, and the other 24 cm. Two identical specimens were placed with their smaller electrodes together to form a test unit. As the outside plates were always kept at earth potential, test units could be placed on top of one another without in any way affecting the electrical measurements. The method of mounting the specimen and attaching the leads is shown diagrammatically in Figure 6.

3. LEADS

There was one lead, kept at earth potential, which was common to all the units. It consisted of a brass rod extending through the cover near its outer edge and reaching nearly to the bottom of the chamber. In addition, each specimen had two leads, symmetrically placed with respect to the common lead; these two leads will be called the measuring lead and the dummy lead. This latter is to aid in measuring lead capacitance. These likewise consisted of brass rods similar to the common lead. All the leads were insulated not alone by the hard rubber top, but also by passing each of them through a plug of paraffin.

Between each unit, and at the top and at the bottom of the assembly, were placed plates of metal in the form of a disk with a projection. These projections served to connect the plates to the common lead. Between the two specimens of each unit was placed a small disk of metal, about 18 cm in diameter, with a projection sufficiently long to reach the measuring lead of that specimen. A piece of metal exactly like this projection was attached to the corre-

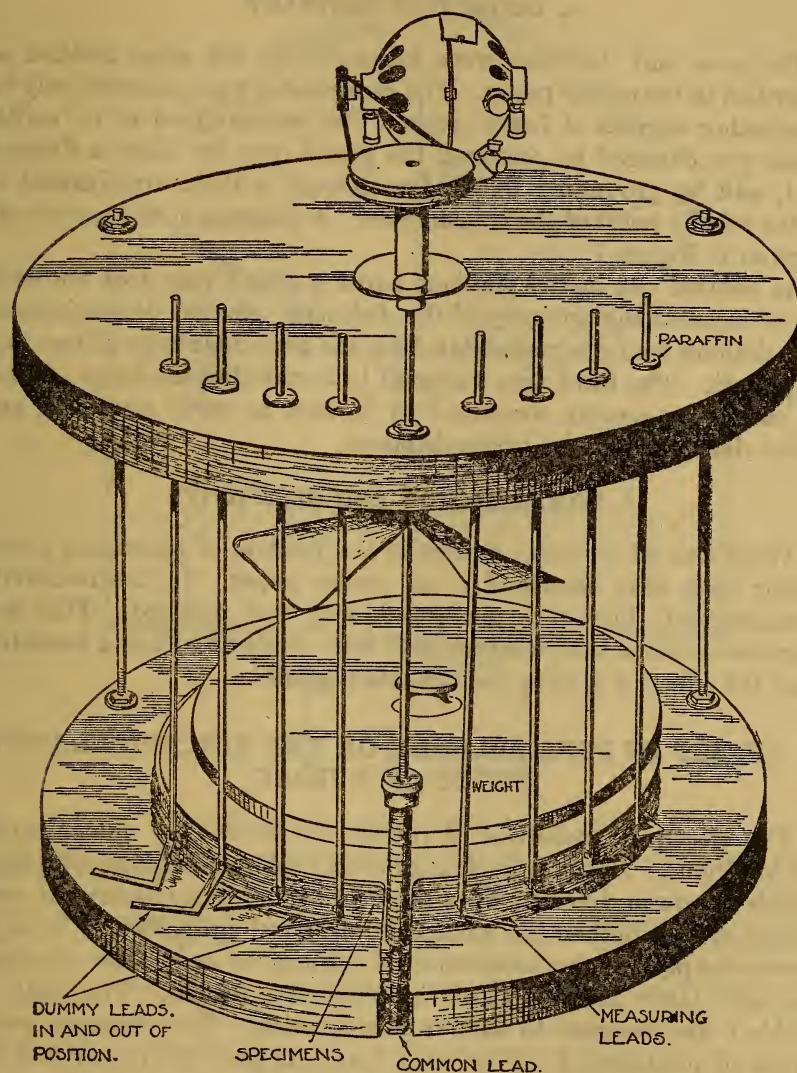


FIG. 6.—Specimens mounted for electrical measurement

Specimens are mounted on a hard-rubber disk suspended from the cover of the constant temperature chamber. The cover is then sealed in place in the jar which constitutes the chamber. Measurements are made after the temperature and humidity become constant. The specimens are connected to the measuring bridge by the vertical brass rods.

sponding dummy lead, and placed in a position similar to that occupied by the projection.

4. DIELECTRIC CONSTANT

The area and thickness were measured by the same method as described in the earlier paper. The capacitance was measured only by alternating current of 1,000 cycles. The set-up given in an earlier paper was changed by omitting the guard ring, by using a dummy lead, and by grounding the bridge through a third arm instead of at the middle point of the transformer. A diagram of the new set-up is given in Figure 7.

As pointed out in the previous paper a guard ring does not ordinarily increase the accuracy of the dielectric constant determination. The dummy lead was necessitated by the particular type of test unit employed. The third arm was used to insure that the large number of leads permanently connected to H were at earth potential, and hence did not alter the bridge balance.

5. POWER FACTOR AND RESISTIVITY

There was no essential change in the method of measuring power factor from that described in an earlier paper. In the resistivity measurement, however, the guard ring was omitted. This was permissible since the measurements were made at so low a humidity that the effect of surface leakage was negligible.

V. EFFECT OF FREE SULPHUR ON THE ELECTRICAL PROPERTIES OF RUBBER

The electrical properties of rubber are altered by vulcanization with sulphur. But inasmuch as sulphur itself has electrical constants which are quite different from those of rubber, the question at once arises as to whether the change in electrical properties is brought about simply by the admixture of sulphur or only after chemical reaction takes place between sulphur and rubber. The data in Table 6 are designed to answer this question. The electrical properties of mixtures of rubber with 8 and 32 per cent of sulphur are practically identical with those of crude rubber, but are different in every respect from those of the same compounds after vulcanization. For convenient comparison the properties of a compound containing 2 per cent of combined sulphur is shown in the same table. The properties of rubber are changed more by vulcanizing with 2 per cent of sulphur than they are by the admixing of 32 per cent of sulphur.

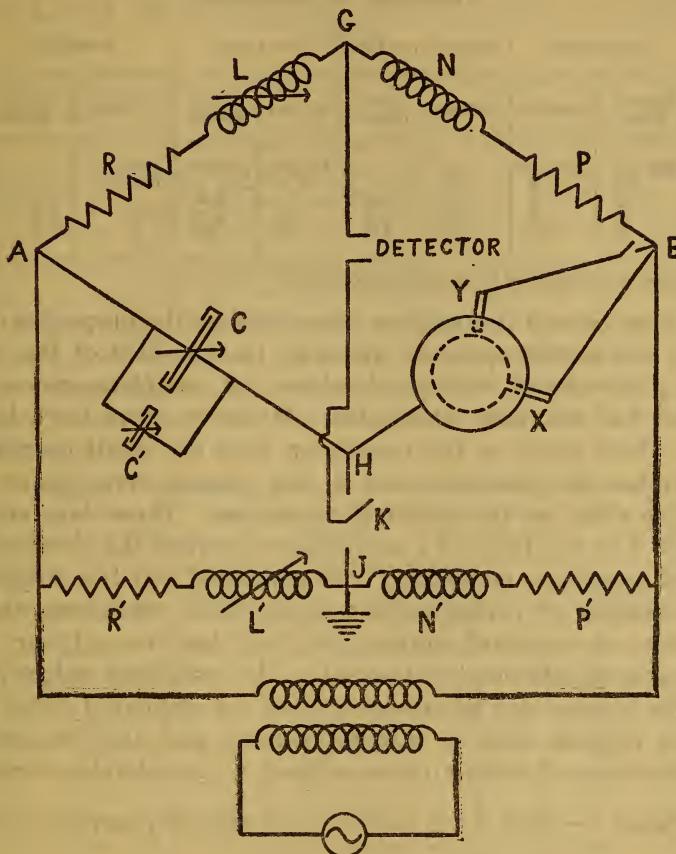


FIG. 7.—Diagram of the modified Rosa bridge

To make a measurement of the capacitance and the power factor several cycles of adjustments must be made in which the detector is connected first to the bridge and then to the third arm. First connect the specimen not only by its regular lead, but also by the dummy lead Y . The cycle consists in first connecting K to H , and balancing by adjusting C and L , then connecting K to J , and balancing by adjusting R' and L' . This cycle is repeated until the throwing of K from J to H does not affect the balance of either the bridge or the third arm. Let the reading of the left-hand inductance be L_1 . Substitute for the specimen a calibrated condenser S having a lead of known capacitance. Make another cycle of adjustments varying S and L when adjusting the bridge, and R' and L' when adjusting the third arm. Let the readings of the calibrated condenser and the left-hand inductance be S_1 and L_2 . Connect the specimen into the bridge as before with the exception of the dummy lead Y which is disconnected not only at B , but also at the specimen. The disconnection at the specimen is accomplished by turning the brass rod through 90° . Adjust the bridge in the same way as when both leads were connected. Let the reading of the left-hand inductance be L_3 . Again substitute the calibrated condenser for the specimen and make the cycles of adjustments. Let the reading of the calibrated condenser be S_2 . The reading of the inductance will be L_4 as before. The capacitance of the dummy lead and hence of the measuring lead is $S_1 - S_2$. The capacitance of the specimen is $S_2 - (S_1 - S_2)$. If $L_1 = L_3$, as is usually the case, and $R_1 = P_1$, the power factor F is given with sufficient approximation by the equation

$$F = \frac{p(L_1 - L_4)}{R_1}$$

where p is 2π times the frequency of the alternating current used in the measurement, and R_1 and P_1 are the total resistances of the arms AG and BG .

TABLE 6.—Comparison of the electrical constants of rubber-sulphur mixtures with rubber-sulphur compounds¹

Composition		Dielectric constant		Power factor		Resistivity	
Smoked sheet	Sulphur	Mixture	Compound	Mixture	Compound	Mixture	Compound
Per cent	Per cent			Per cent	Per cent	Ohm-cm	
100	0	2.53		0.19		0.3×10^{15}	
98	2		2.67		0.31		3.3×10^{15}
92	8	2.58	3.56	.24	1.28	1.8	3.8
68	32	2.51	2.91	.20	.82	.2	20.0

¹ All samples were vulcanized for about 600 minutes at 160° C.

But even though free sulphur does not alter the properties of crude rubber, the further question arises as to the effect of free sulphur on the properties of vulcanized rubber. A complete answer to this question has not been attempted. However, data have been obtained which point to the conclusion that the small proportion of free sulphur in specimens used in the present investigation had a negligible effect on the electrical properties. These data are shown in Table 7 in the form of a comparison between the electrical properties of specimens containing both combined and free sulphur with the properties of rubber-sulphur compounds containing the same proportion of combined sulphur, but very low free sulphur. Much significance should not be attached to the resistivity values given in the table because the compositions that are compared differ slightly in other respects than in sulphur content, and also because single determinations of resistivity are subject to considerable variation.

TABLE 7.—Effect of free sulphur on the electrical properties of rubber

Sulphur content		Dielectric constant	Power factor	Resistivity
Combined	Free			
Per cent	Per cent			
0.9	31.0	2.51	0.18	1.0×10^{15}
.9	<.1	2.56	.25	3.2
4.7	27.2	2.97	.81	1.3
4.7	<.1	3.11	.40	3.4
9.3	22.6	3.58	2.55	.6
9.3	<.1	3.70	2.25	4.2
14.6	17.3	3.06	7.5	7.7
14.6	<.1	3.26	7.1	8.0

Specimens containing the large proportions of free sulphur were prepared from a stock of the following composition:

	Parts
Rubber	68
Sulphur	32
Zinc oxide	1
Tetramethylthiuramdisulphide	1

The comparison data were obtained from the curves in Figures 8, 9, and 10.

VI. RELATION OF ELECTRICAL PROPERTIES TO COMPOSITION

As has already been indicated the chief emphasis in this investigation was placed on measurement of the electrical properties of compounds of rubber and sulphur, rather than of mixtures of rubber and sulphur, or of rubber-sulphur compounds and sulphur. A summary of the electrical measurements on compounds of rubber and sulphur is given in Table 8. For many compositions there are specimens cured at different times and temperatures. Inasmuch as the varying conditions of cure all led to substantially complete combination of rubber and sulphur, the results are grouped and averaged together on the basis of composition. The time and temperature of vulcanization have no significant influence beyond their effect on the state of combination of rubber and sulphur, except perhaps, in connection with the resistivity.

TABLE 8.—*Electrical constants of rubber-sulphur compounds*

Composition		Vulcanization		Dielectric constant		Power factor		Resistivity	
Rubber	Sulphur	Time	Temperature	Individual determinations	Mean	Individual determinations	Mean	Individual determinations	Mean
Per cent 100	Per cent 0	Minutes	° C.	2.55 2.55 2.41 2.66 2.32 2.35 2.42 2.36	2.45	0.19 .19 .20 .19 .19 .17 .15 .16	.19 .30 .31	3.1×10 ¹⁵ 3.4 3.4 3.1 3.0 1.0 1.0 1.0	2.4×10 ¹⁵
98	2	360	160	2.67 2.67		.32 .30	.31	3.3 3.2	3.3
97	3	600	160	2.85 2.83	2.84	.36 .36	.36	3.6 3.3	3.5
96	4	360	160			.35 .35	.35	3.0 3.7	3.4
94	6	600	160	3.30 3.34	3.32	.55 .55	.55	3.9 3.8	3.9
92	8	360	160	3.59 3.57 3.54 3.55	3.56	1.37 1.41 1.17 1.17	1.28	3.5 2.5 2.5 4.5	3.3
91	9	360 600	160	3.63 3.60	3.62	2.01 2.05	2.03	4.6 2.8	3.7
90	10	600 360 600 250 160 150	160 141 150 160 160 150	3.76 3.77 3.74 3.70 3.67 3.61		3.22 3.07 3.50 3.30 4.39 3.62		4.4 5.2 10.4 10.9 4.8 4.8	
		300 600 300	150 141 160	3.68 3.64 3.82		3.56 2.14 3.62		4.8 7.7 7.0 4.5	
				3.79	3.74	3.53	3.38	4.6	6.2
89	11	360	160	3.77 3.73	3.75	5.13 5.37	5.25	4.0 4.0	4.0

TABLE 8.—*Electrical constants of rubber-sulphur compounds—Continued*

Composition		Vulcanization		Dielectric constant		Power factor		Resistivity	
Rubber	Sulphur	Time	Temperature	Individual determinations	Mean	Individual determinations	Mean	Individual determinations	Mean
<i>Per cent</i>	<i>Per cent</i>	<i>Minutes</i>	<i>° C.</i>			<i>Per cent</i>	<i>Per cent</i>	<i>Ohm-cm</i>	<i>Ohm-cm</i>
88	12	360	160	3.89		6.58		3.8×10^{15}	
		600		3.81		6.92		7.3	
		600	155	3.65		7.37		10.3	
		80	160	3.72		(4.27)		6.5	
		160		3.66		6.79		(71.)	
		250	150	3.59		5.99		(28.4)	
		600	141	3.74	3.72	6.48	6.60	(26.8)	7.0×10^{15}
87	13	80	160	3.54		5.17		6.0	
		250	155	3.70		7.45		13.3	
		600	141	3.83		4.48		7.9	
		80	160	3.77		6.42		5.3	
		160		3.66		8.19		8.2	
		240		3.64		8.52		7.4	
		160		3.50		8.06		5.4	
		150		3.65		8.01		8.1	
		300		3.63		8.53		9.2	
		300		3.77		7.12		8.9	
		600	150	3.65		8.30		8.7	
				3.64	3.67	8.35	7.36	9.8	8.20
86	14	80	160	3.57		2.26		4.3	
		160		3.31		8.50		7.1	
		360		3.19		7.44		7.1	
		420		3.21		6.55		3.6	
		600		3.12		6.91		5.4	
		250	150	3.65		7.97		15.0	
		600	141	3.57	3.37	6.48	7.31	17.7	8.6
84	16	420	160	3.04		4.40		3.4	
				2.73		3.63		4.0	
				2.85		5.07		3.3	
		300		3.00		4.31		5.5	
		160		3.05		6.31		10.1	
		150		3.05		4.89		6.0	
		600	155	3.28		7.40		6.4	
		250	150	2.85		6.68		13.2	
		600	141	2.86	2.97	3.36	5.12	4.7	6.3
82	18	420	160	2.86		1.15		3.2	
				2.77	2.82	1.29	1.22	2.5	2.9
81	19	600	155	2.74		.39		6.9	
				2.78		.42		10.6	
				2.77		.36		7.2	
				2.78		.36		10.4	
				2.77		.39		11.9	
				2.77	2.77	.37	.38	10.5	9.6
80	20	420	160	2.81		.42		11.1	
78	22	420	160	2.85		.35		11.9	
78	24	600	150	2.81		.49		16.8	
				2.82		.83		31.4	
				2.82		.82		24.0	
				2.85	2.82	.64	.70	47.3	30.0
71.5	28.5	600	155	2.88		.82		35.2	
				2.90		(2.44)		32.6	
				2.89		.56		31.0	
				2.88		.73		35.1	
				2.88		.85		25.9	
				2.87	2.88	.47	.68	27.7	31.2
68	32	600	150	2.90		1.01		17.1	
				2.89		.92		24.7	
				2.91		.86		21.1	
				2.89		.79		23.5	
				2.82	2.90	.83	.88	22.9	21.9

1. DIELECTRIC CONSTANT

The manner in which the dielectric constant varies with the proportion of sulphur is shown by Figure 8. From the beginning of vulcanization, the dielectric constant increases rapidly with increasing percentage of sulphur in the range of composition of ordinary soft-rubber compounds. It passes through a maximum at about 10.5 per cent of sulphur and has a value at this point of 3.75. This represents an increase of about 50 per cent over the dielectric con-

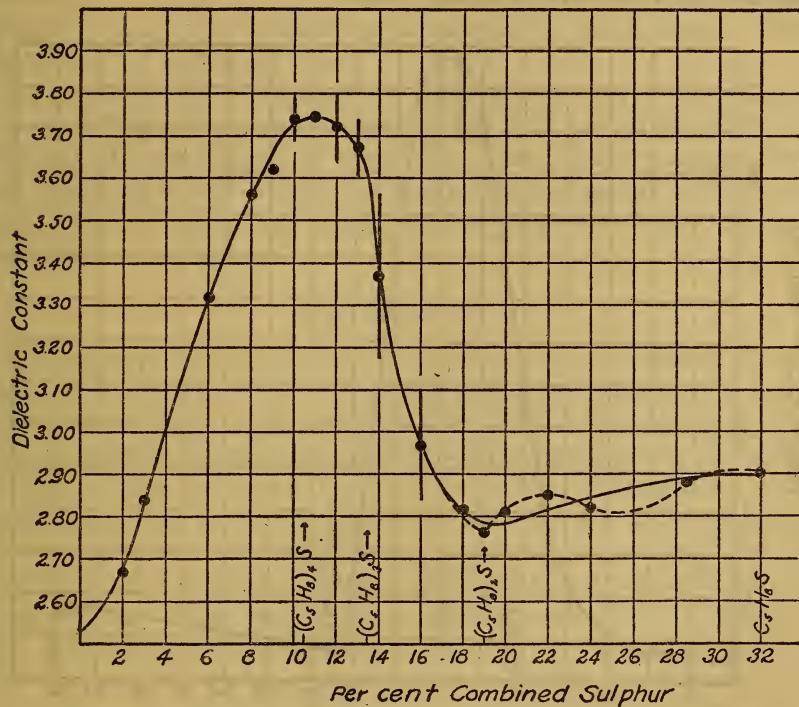


FIG. 8.—Curve showing the relation of the dielectric constant to the per cent of sulphur

The dots indicate the mean value at each composition. The vertical lines through the dots indicate the average derivation from the mean of several observations.

stant of crude rubber. After passing through the maximum, the dielectric constant decreases rapidly with increasing percentage of sulphur and comes to a minimum value at the composition 19 per cent of sulphur. At this point the dielectric constant is 2.77, which is only about 10 per cent higher than the dielectric constant of crude rubber, and is equivalent to that of soft rubber containing about 3 per cent of sulphur. From 19 to 32 per cent sulphur, a range of composition which includes hard rubber, the dielectric constant undergoes a slight, but definite, increase from about 2.8 to 2.9, having the

latter value for rubber containing the maximum proportion of sulphur with which it is capable of combining.

The vertical lines which are drawn through each point on the curve indicate the average deviation from the mean of determinations at that composition. For soft-rubber and for hard-rubber compounds the consistency of results is that which might be expected from reasonable care in compounding and in making electrical measurements; the deviations are quite small. However, for intermediate compositions the variations are relatively large.

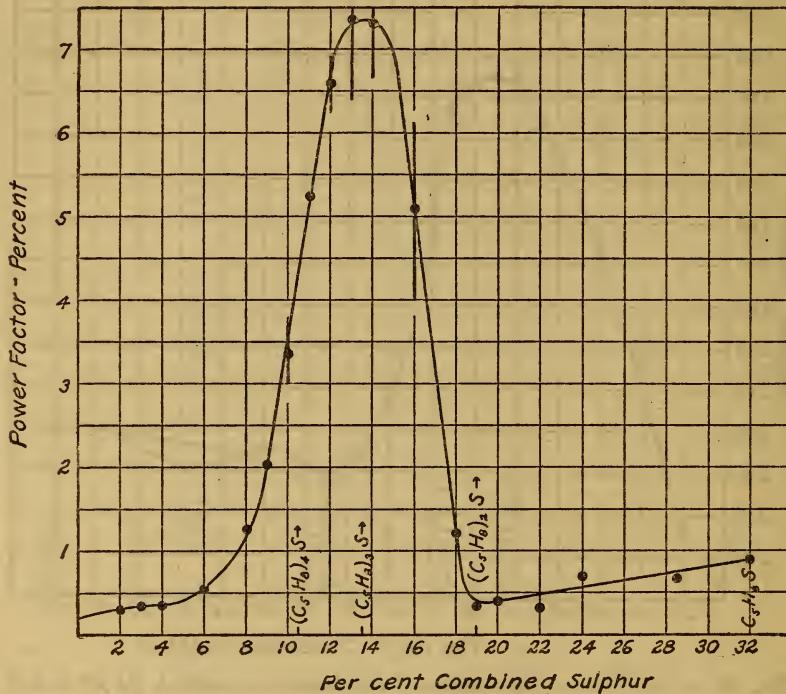


FIG. 9.—Curve showing the relation of the power factor to the per cent of sulphur

The dots indicate the mean value at each composition. The vertical lines through the dots indicate the average derivation from the mean of several observations.

2. POWER FACTOR

As shown in Figure 9, the variation of the power factor with the composition partakes of the same general nature as the variation of the dielectric constant with composition. The curves, however, are not identical in shape, and the magnitude of the variation of the power factor is about thirtyfold, as compared with 50 per cent for the dielectric constant. The power factor of crude rubber is about 0.2 per cent. The power factor does not change in uniform manner from its initial to its maximum value. Up to about 6 per cent sulphur

the increase in power factor is quite small in comparison to the increase from this point to 13 per cent. The maximum occurs at 13 per cent of sulphur instead of between 10 and 11 per cent as is the case for the dielectric constant. The power factor at the maximum has the high value of 7 per cent, corresponding to a phase difference of 4° . After passing the maximum, the power factor undergoes a very rapid decrease and reaches its minimum value at 19 per cent of sulphur, just as does the dielectric constant. Throughout the range of hard-rubber compositions, the power factor increases with the percentage of sulphur in much the same manner as the dielectric constant, though the proportionate increase is much larger, being from about 0.4 to 0.9 per cent.

The power factor determinations show the same type of variation between individual values that was observed in case of the dielectric constant. In the regions in which the power factor changes little with composition the values are uniformly consistent, but in the region of high values and rapid change of power factor, marked instability is encountered.

3. RESISTIVITY

The resistivity of insulating materials, such as rubber, is not related to the composition in as simple and direct a manner as is the dielectric constant. It is probable that small proportions or even traces of constituents have more to do with the conduction of current through a given specimen than do the main constituents. Consequently, it is not surprising that there are relatively wide variations between individual determinations of resistivity on specimens of the same rubber and sulphur content. The data, as plotted on Figure 10, do not define a sharp, smooth curve relating resistivity to composition. The solid curve was drawn to represent the relation of resistivity to composition with no regard for the possible interpretation of the results. The dotted portion of the curve was drawn subsequently in order to better fit the observations and also to indicate more clearly the possible evidences for the existence of definite compounds between rubber and sulphur. But, whatever the exact shape of the curve, the outstanding feature is the fact that it is made up of two distinct portions, the first, from 0 to 19 per cent of sulphur, being lower than the second, from 19 to 32 per cent. The resistivity of crude rubber is approximately 3×10^{15} ohm-cm, and this same value obtains over the range of ordinary, soft, vulcanized rubber and up to nearly 10 per cent of sulphur. From 10 to 14 per cent of sulphur the resistivity shows a decided increase, but it in no way goes through high values similar to those that have been noted in this range for the dielectric constant and the power factor. There is a change in direction of the curve near the composition, 14 per cent of sulphur which may be

a low maximum. There is another change in direction, which is possibly a minimum, near the composition, 19 per cent of sulphur, just before the curve takes the sudden upward trend. The high values at 24 and 28.5 per cent of sulphur indicate a maximum somewhere near 26 per cent, though there are no determinations at this exact composition. The resistivity undergoes a decrease between 28.5 and 32 per cent of sulphur. At the latter composition the resistivity is of the order, 20×10^{15} ohm-cm, or about seven times as great as for crude rubber.

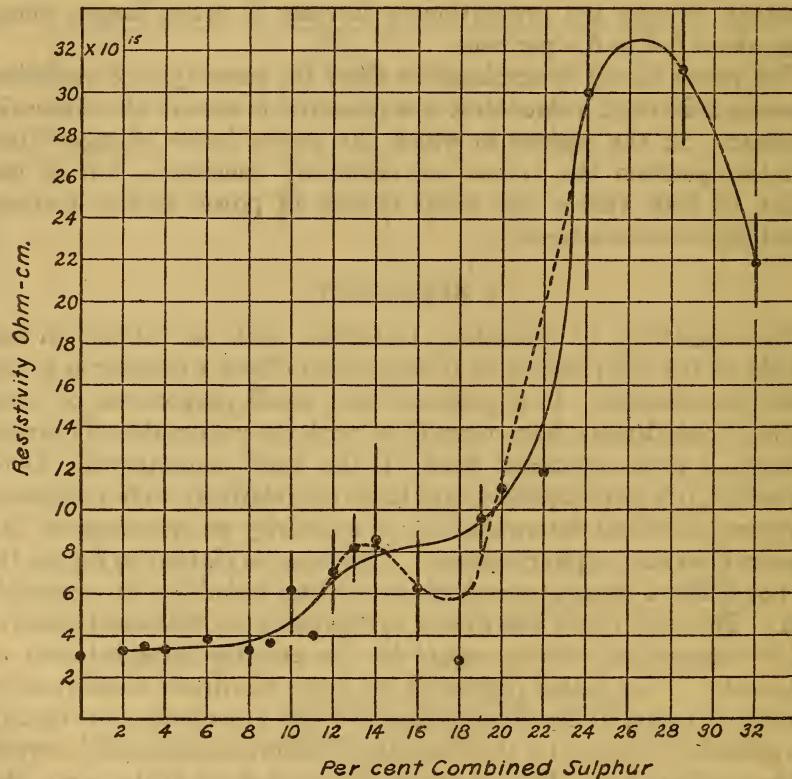


FIG. 10.—Curve showing the relation of the resistivity to the per cent of sulphur

The dots indicate the mean value at each composition. The vertical lines through the dots indicate the average derivation from the mean of several observations.

4. DIELECTRIC STRENGTH

Many of the specimens that were used for measurement of the previously discussed electrical properties were subjected to electrical breakdown after the other tests had been completed. The results showed considerable variation between individual determinations, as is characteristic of electrical breakdown, even when all circumstances are kept as nearly constant as possible. While there did appear to be

some relation between composition and dielectric strength, factors other than the composition, such as dimensions of the specimen, temperature, frequency, and rate of applying potential gave rise to variations of much larger magnitude. It was concluded that any worthwhile knowledge of the breakdown of rubber-sulphur compounds must wait on a more adequate knowledge of the nature of electrical breakdown and of the method of measuring it.

VII. INTERPRETATION OF THE RESULTS

The salient feature of the changes in electrical properties is that they all occur at compositions which may be represented by simple formulas. This is well shown by the summary which is given in Table 9. Results from the investigation of the density of rubber-sulphur compounds are included with the electrical properties. The agreement of the changes with definite formulas suggests at once the interpretation of the results on the basis of the formation of simple chemical compounds by the interaction of rubber and sulphur. The relation of electrical properties to chemical composition is not well known. A single change or break in the curve relating one property to the composition would be of doubtful significance, but the fact that all of the observed changes in electrical properties and in density occur at compositions which correspond to four simple formulas gives assurance that compound formation is the fundamental basis for the interpretation of the observed changes.

TABLE 9.—*Summary of evidence for the existence of definite compounds of rubber and sulphur from changes in curves representing the changes in the properties with composition*

Empirical formula	Sulphur	Dielectric constant	Power factor	Resistivity	Density	Coefficient of thermal expansion
$(C_6H_5)_4S$ -----	Per cent 10.5	Maximum	No indication.	Direction change.	No indication-----	No indication.
$(C_6H_5)_3S^1$ -----	13.5	No indication.	Maximum	do-----	do-----	Do.
$(C_6H_5)_2S$ -----	19	Minimum	Minimum	do-----	Direction change.	Direction change.
$(C_6H_5)_3S_2$ -----	26	No indication.	No indication.	Maximum-----	No indication-----	No indication.
$(C_6H_5)S$ -----	32	Existence of compound	generally recognized from chemical evidence.			

¹ Equivalent to $(C_6H_5)_4S \cdot (C_6H_5)_2S$.

One of the electrical properties, resistivity, seems to depend less on the amount of rubber and sulphur in a given compound than on other factors, such as the physical state of the material, and the presence of small proportions of constituents other than rubber and sulphur. In some measure all of the changes in electrical properties may be correlated with the physical state of the material, but this does not necessarily minimize their dependence on the chemical composition.

1. FORMATION OF DEFINITE CHEMICAL COMPOUNDS

As indicated in Table 9, the dielectric constant, power factor, resistivity, molecular volume, and thermal expansivity all show changes at the composition 19 per cent of sulphur, which corresponds to the formula $(C_5H_8)_2S$. At this composition the dielectric constant and power factor curves pass through well-defined minima, the resistivity shows a decided increase and there is a distinct break in the curve which relates molar volume to composition. The coefficient of thermal expansion also undergoes a large change at this composition. Other properties as well show distinct changes at this same composition. In connection with measurements of the tensile properties of hard rubber, Glancy and coworkers⁶ found that "rapid changes take place in the physical properties of a rubber-sulphur mixture when the coefficient of vulcanization reached approximately 23.5, or apparently when each $C_{10}H_{16}$ group has received one atom of sulphur to form polyprene monosulphide." Whitby and Jane⁷ found that sulphur could be removed from hard rubber, C_5H_8S , by reaction with alcoholic alkali until a composition containing 19 per cent of sulphur was obtained. While they did not regard this as adequate evidence to establish the existence of a definite compound $(C_5H_8)_2S$, it is highly significant when taken in conjunction with the changes in physical and electrical properties. Thus, there is a variety of evidence that the formula $(C_5H_8)_2S$ represents a definite chemical compound.

The evidence for the existence of other definite compounds of rubber and sulphur is not so comprehensive or so complete as for the above-mentioned compound. No other one composition marks changes in all of the physical properties studied. However, some of the physical properties undergo distinct changes at each of the three other compositions indicated in the table. The maximum value of the dielectric constant occurs at the composition $(C_5H_8)_4S$. The resistivity curve shows only a relatively small change at this composition, while other properties give no indication. More precise data, particularly in case of the density and the thermal expansivity, might give definite evidence for a compound at this composition. A maximum value of the dielectric constant constitutes strong evidence for compound formation because the dielectric constant of mixtures is usually intermediate between that of the components, so that a maximum value could come about not from a fortuitous mixture but only from the formation of a definite compound.

The power factor goes through a maximum value at the composition $(C_5H_8)_3S$ and the resistivity shows a small change at the same

⁶ W. E. Glancy, D. D. Wright, and K. H. Oon, "Rate of combination of sulphur with rubber in hard rubber," *J. Ind. Eng. Chem.*, **18**, p. 73; 1926.

⁷ George Stafford Whitby and Robert Stephen Jane, *Trans. Royal Society, Canada (3)*, **20**, p. 121; 1926.

point. So far as present evidence is concerned, this composition may represent a definite compound, or it may be equivalent to a mixture of equimolecular proportions of $(C_5H_8)_4S$ and $(C_5H_8)_2S$. Unlike the case of the dielectric constant, there is no basis on which to say whether a maximum power factor is associated with a mixture or with a definite compound.

The maximum value of the resistivity occurs in the range of hard-rubber compositions, at about 26 per cent of sulphur, which corresponds to the formula $(C_5H_8)_4S_2$. Careful examination of the dielectric constant curve as given in Figure 8 indicates a minimum also at this composition, but of a magnitude scarcely greater than the possible experimental error. This is shown on the curve by a dotted line. The density relations undergo no distinct change at this composition, but here, as for $(C_5H_8)_4S$ and $(C_5H_8)_3S$, it should not be regarded as negative, but rather as inconclusive evidence since determinations of the density are not in perfect accord with a simple linear relation through this region, yet they are not adequate to define the exact relation which may exist.

All of the evidence for compound formation which has been here elaborated is in accord with what was pointed out in the introduction as the expected course of the reaction between rubber and sulphur. Here as in the introduction no specific molecular structure has been assumed for the molecule of rubber hydrocarbon.

It is not to be supposed that the simple, definite compounds of rubber and sulphur which are here discussed are produced in a pure state when the components react in the proportions that are indicated by the formulas. On the contrary, it is very probable that the reaction products are at all times mixtures of molecular species having quite an appreciable range of composition. This being the case, not all properties would be expected to be definitely characteristic for all compounds.

VIII. CONCLUSIONS

The electrical properties of rubber-sulphur compounds depend primarily upon the percentage of sulphur in combination with the rubber. Free sulphur has a relatively small effect on the electrical properties.

As the combined sulphur in vulcanized rubber is increased from 0 to 32 per cent, the electrical properties show the following changes:

The dielectric constant increases until a maximum value is reached at 10.5 per cent of combined sulphur, decreases to 19 per cent and then increases slightly from this composition to 32 per cent.

The power factor behaves similarly, except that the maximum value comes at 13 per cent of combined sulphur.

The resistivity increases up to a maximum at 26 per cent and decreases from this point to 32 per cent of combined sulphur. The

curve shows reasonably distinct changes in direction at approximately 10.5, 13.5, and 19 per cent of combined sulphur.

The electrical breakdown is affected to such an extent by the circumstances of test that no reliable conclusions can be drawn from present data as to the effect of varying sulphur content in this property.

It is noteworthy that all of these changes, as well as changes in the density relations, occur at compositions which may be represented by simple formulas. The existence of a definite compound of empirical formula $(C_5H_8)_2S$ is indicated by all of the properties which have been studied. The evidence for three other compounds $(C_5H_8)_4S$, $(C_5H_8)_3S$, and $(C_5H_8)_4S_3$ is less complete. The idea of the formation of definite compounds in the reaction of sulphur with rubber is in accord with well-established principles of organic chemistry.

WASHINGTON, May 17, 1927.



AUTHOR Scientific Papers of
the Bureau of Standards
Vol. 22
OWNER'S NAME

